

Structure of a Lamellar Fluid under Confinement & Shear Studied using the Second Generation X-ray Surface Forces Apparatus (XSFA-II) and X-ray Micro-diffraction

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ABSTRACT The structure of a fluid membrane system composed of surfactant-co-surfactant-oil-water mixtures has been investigated under confinement and shear conditions. Small Angle X-ray Scattering (SAXS) was employed with a second generation X-ray Surface Forces Apparatus (XSFA-II) to study the time evolution of the orientational structure of the lamellar fluid under oscillatory shear. In a regime of relatively big confinement gap ($\sim 800\text{ }\mu\text{m}$) and small shear amplitude ($\sim 40\text{ }\mu\text{m}$), we observed for the first time direct evidence of an “orientational phase separation” behavior, where a surface boundary layer adopts different orientation and separates from the bulk region. Under continuous shearing, the surface boundary layer grows in thickness and aligns towards a shear-favored (low friction) state while the bulk orientation remains unchanged. To further investigate the effects of surface confinement, we spatially mapped, in $\sim 1\text{ }\mu\text{m}$ sections, the orientation structure of the lamellar fluid sample confined between two glass surfaces using a micro-focused x-ray beam produced by a linear Bragg-Fresnel Lens at the Advanced Photon Source. The data confirmed the expected trend that the smectic domains align progressively better with respect to the surface as they approach the surface.

Key Word: Complex Fluids, Confinement, Surface Forces, X-ray Micro-diffraction

1. Introduction

The structure of complex fluids under confinement and shear has been studied extensively in the last twenty years. These studies have fundamental aspects in, e.g., correlating lateral force features with structural transitions, as well as practical implications such as designing novel

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lubricants based on structured molecular fluids. The visco-elastic properties of these structured fluids were found to be highly dependent on the molecular orientation. In fluids where the molecules are either arranged in layers (smectic or lamellar phase) or as hexagonal arrays of cylindrical micelles, very low frictional forces were measured [1]. This has been attributed to molecules realigning under shear to low frictional states, such as the "sliding layer" arrangement in the lamellar phase and the "rolling cylinder" arrangement in the hexagonal phase. The development of techniques that can directly probe structural and chemical evolution in shearing contacts at real-time is essential for understanding this and other complicated tribological processes. Earlier work using a x-ray Couette shear cell has shed some light on the structure of bulk molecular fluids under shear [2,3]. For measurements of confined thin films, the X-ray Surface Forces Apparatus (XSFA)[4,5], adapted directly from the SFA-III surface forces apparatus[6], is an ideal tool because of its capability to measure structural changes in the sample upon shear at well-defined gap separations.

Recent developments have led to the second generation X-ray Surface Forces Apparatus (XSFA-II), with normal and shear force measurement capabilities coupled with *in-situ* small angle x-ray scattering experiments under static confinement and oscillatory shear conditions in a well-defined environment. The results of the first study using the XSFA-II of the dynamical evolution of the orientational structure of a four-component lyotropic membrane fluid system under shear are presented here. In these experiments the x-rays impinge on the sample in the direction normal to the confining surfaces, therefore giving orientation information about the lamellar domains normal to the surfaces.

Using a micro-focused x-ray beam in the glancing incidence geometry, measurements were made on the same sample system confined between glass surfaces in a rectangular capillary. These measurements are complementary to the XSFA studies and provide the orientation structure of the smectic layers parallel to the confining surfaces. More importantly, the $\sim 1\ \mu\text{m}$ size focused beam, which was produced using a Bragg-Fresnel Lens at the Advanced Photon Source, a third generation synchrotron, enabled us to spatially map the orientational profile of the sample in thin (comparable to beam size) sections. This makes possible the visualization of surface effects on domain orientations as a function of the distance from the surface.

2. Materials

The samples we studied consisted of mixtures of Sodium Dodecyl Sulfate (SDS, surfactant), Pentanol (co-surfactant), Dodecane(oil) and water. This system has a well characterized, rich phase diagram [7], which allows us to access a variety of molecular structures by changing the composition. For the experiments described here, we focused on samples in the L_α (lamellar) phase. In this phase region, because the molecules are arranged in stacked layers which are intrinsically anisotropic, the application of confining surfaces or external shear is expected to induce re-arrangement of domains into energetically favorable (low friction) structures.

3. Results from XSFA-II Studies

The second generation X-ray Surface Forces Apparatus (XSFA-II) is schematically illustrated in Fig. 1. The completely redesigned sealed sample chamber has three windows to allow

simultaneous coaxial optical and x-ray measurements. Incident and scattered x-rays are transmitted through an ultra-thin (50 μm) Silica front window and a Beryllium back window, both of which have low x-ray absorption. The visible light signal is separated from the x-rays by a mirror and passed through a photo-spectrometer for monitoring the gap using FECO fringes (gap size down to angstrom level has been achieved). A side port allows direct sample injection in between the two confining surfaces from outside of the sample chamber. Humidity control is achieved by using a reservoir feedthrough on the housing. The surfaces are made of quartz-backed mica mounted on curved Aluminum disks [8]. Temperature and humidity sensors can be incorporated into the housing. A friction device attached to the front side of the apparatus measures the frictional force between the two surfaces in tandem with optical and x-ray measurements.

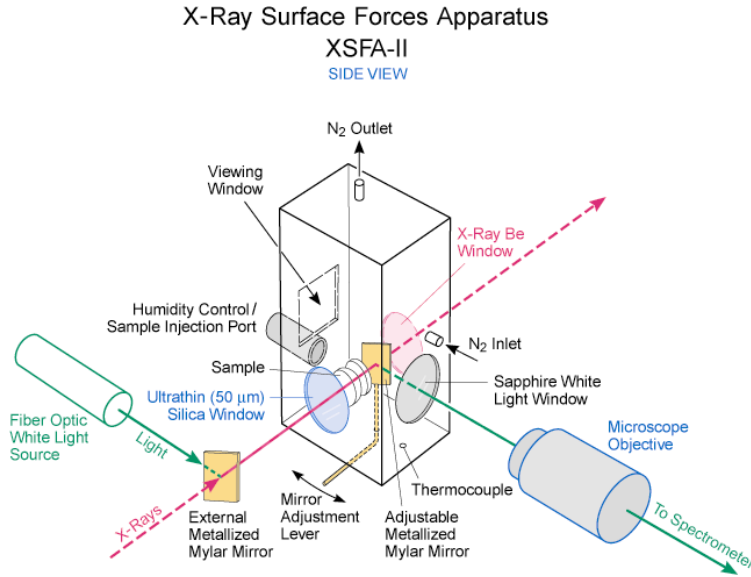


Fig. 1 Schematic drawing of the XSFA-II.

The experiments were carried out using a 18 kW Rigaku rotating anode x-ray source ($\lambda = 1.54$ Å) and a small angle x-ray spectrometer with a 2-D image plate detector. The beam size on the sample was 0.5 mm x 0.5 mm. We had chosen to study the behavior of these lamellar fluid samples in fairly large gaps (~ 800 μm) in order to maximize x-ray scattering signal. Two x-ray diffraction patterns from a lamellar sample under static and shear conditions are shown in Fig. 2. The ring of scattering intensity corresponds to the first order (001) peak of the smectic layer spacing. A uniform ring would suggest isotropically distributed membrane domains. Clearly, even when the sample was initially injected in between the surfaces (static data), the surface confinement effects were already aligning the smectic domains in preferred orientations, which varied between different fillings of the sample. The direction where the scattering is strongest indicates the preferred orientation (indicated by the lines in the images) of the plane normal of the smectic layers. Fig. 2 c illustrates the three possible real space orientations, labeled “a”, “b”, “c”, respectively, of the smectic layers with respect to shear. In the data shown in Fig. 2 a (no shear), the surfaces are oriented parallel to the plane of the image, and the preferred orientation is close to the “b” orientation at $\phi = 0$, which is the direction of shear. The “b” orientation is a high

friction state and is generally forbidden at high shear rates [2].

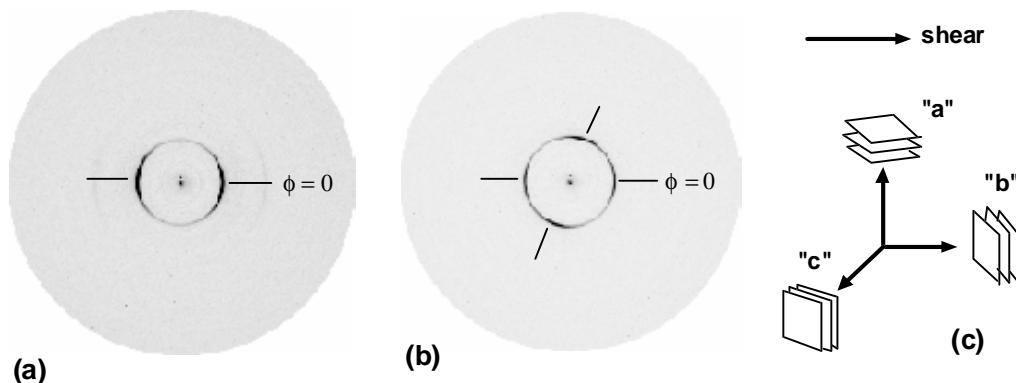


Fig. 2 X-ray diffraction patterns collected using the XSFA-II from a SDS lamellar sample (a,b). Data shown in (a) was taken at static (no shear) condition, whereas (b) is the 2-D diffraction data of the same sample after 15 hours of shear. The three possible real space orientations of the lamellar layer with respect to the shear surface are defined in (c).

The shear is applied by moving one of the surfaces in the XSFA-II relative to another using a piezoelectric transducer. Because of the limited amplitude in the movement ($\sim 40 \mu\text{m}$ for the experiments) and the large gap size used, the effective shear rate is small. In fact, this shear rate is below what most people have studied before. What is interesting and somewhat surprising is that the sample *did* respond to this perturbatory shearing, albeit on a much slower time scale. Fig. 2 b shows the diffraction pattern from the same sample as in Fig. 2 a, but after 15 hours of oscillatory shearing (frequency = 1 Hz). The data show two populations of the aligned smectic planes, almost orthogonal to each other. Because the data are on the same intensity scale, Fig. 3 b strongly suggests that the initial “b” oriented domains have been redistributed into a combination of “b” and “a” oriented domains. The transition from “b” to “a” orientation makes sense because the “a” orientation is less shear-resistant. Contrary to high shear rate experiments on bulk samples [2], the “b” orientation did not vanish and is therefore not forbidden at this low shear rate (although it’s clearly not favored).

Fortuitously, the long time scale of the orientation transition provided us with the opportunity to study the dynamic behavior of the transition. X-ray diffraction data taken at every half-hour after the onset of shear gave a clear evolutionary picture of the process. In Fig. 3 (left) we show the result of such a time series. The plots are x-ray intensities as a function of the in plane ϕ angle on the ring of the diffraction peak. On a short time scale (< 1 hour after the onset of shear) (top graph), the intensity maximum (I) (the orientation of the domains) shifts slightly towards a larger angle (II), which is consistent with the shear-resistant “b” oriented domains being strained by the shear field and tilting towards the “a” orientation. At some point (1 – 2 hours), a distinct second peak occurs in the diffraction pattern (curve III in middle graph, diagonal arrow), indicating a different domain orientation. It’s important to note that first peak (“b” domains) at this point relaxes back to the original angular position. *We interpret this result as the rupture of the film into two layers: one bulk layer maintaining the initial orientation and the other boundary layer induced by shear* (see Fig. 3 right graph III for a schematic representation).

From there on, the second diffraction peak increases in intensity over time with shear and shifts continuously towards the shear-favored “a” orientation, while the original “b”-oriented peak decreases in intensity correspondingly. This suggests that under continuous shear the boundary layer not only aligns towards the low-friction “a” orientation, but also grows in thickness. This scenario is depicted in graph IV in Fig. 3 (right). To our knowledge this is the first experiment observation of such ‘orientational phase separation’ behavior.

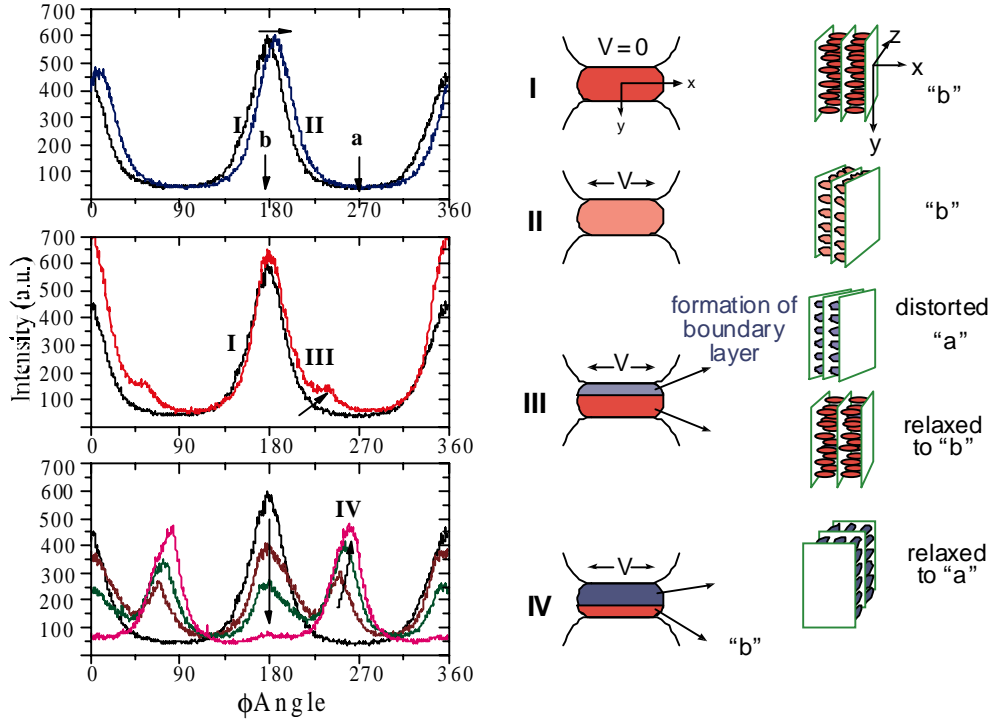


Fig. 3 Time resolved SAXS data showing evolution of the domain orientations (left) and schematic representation of the 'orientational phase separation' model (right). See text for details.

The assumption that the surface layer originates from the moving surface is not an unreasonable one based on the fact that the local shear force is highest at the surface-sample interface. Although the shear amplitude is small compared to the overall gap size, the shear force in the local surface layer apparently was high enough to induce orientation transitions towards the low-friction state. After the separation of the surface layer from the bulk, the shearing force continues to be transmitted to the bulk sample. This explains the gradual propagation over time of the surface layer front into the bulk region. Asymptotically, one expects that the surface layer would occupy the entire gap. The long time scale of this process is a direct consequence of the small shear amplitude. Therefore, this low shear rate case might be considered as a ‘slow motion’ glimpse of what might happen quickly at high shear rates, such as that in the X-ray Couette shear cell where all smectic domains adopt the low friction “a” orientation in a short time[2]. It is likely that the viscosity of the sample had some effects on the formation and propagation of the surface layer. This will be investigated in future experiments by varying the concentration of the membrane in the fluid phase.

4. Results from X-ray Micro-Diffraction

Recent advances in x-ray micro-focusing optics have made available submicron size intense x-ray beams at third generation synchrotron sources, which greatly enhanced the capabilities of hard x-ray microscopy and micro-diffraction methods [9,10]. These microbeams are ideally suited for studying materials under confinement because the microscopic beam size permits spatially resolved structural measurement in the area of interest, e.g., in the confinement gap.

We used a line-focused beam produced using a linear Bragg-Fresnel Lens (BFL) at the Advanced Photon Source to map the orientation profile of the lamellar domains in the SDS sample confined in a rectangular capillary. The diffractive x-ray lenses, developed by us at UCSB, were fabricated by depositing Au (thickness ~ 2000 Å, roughly corresponding to a π phase shift compared to air) in Fresnel zones patterned by electron beam lithography on a (111) Si substrate. This is a much simpler process than the traditional BFL fabrication process based on reactive ion etching methods [9,10]. The optical properties of these novel x-ray micro-lenses, which were characterized before the micro-diffraction experiments, will be described elsewhere.

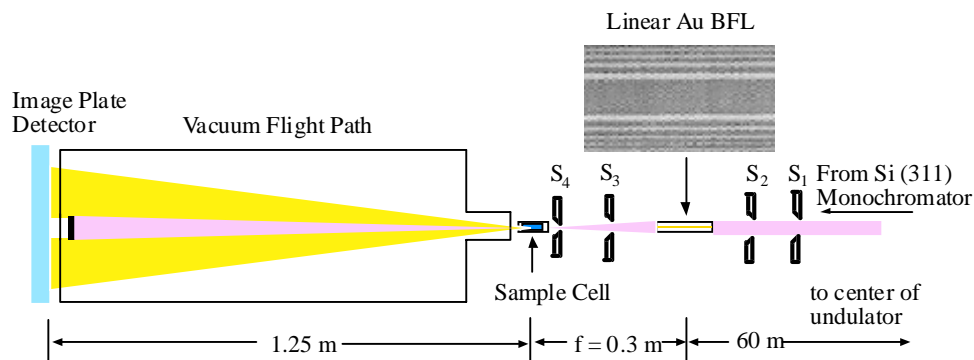


Fig. 4 Illustration of micro-diffraction set up using a linear Bragg-Fresnel Lens at Beamline 2-ID-C at the Advanced Photon Source. Insert: optical microscope image of the linear BFL used in the experiment (only central zones are shown). The diffracted limited resolution of the lens is ~ 0.3 μm (aperture = 0.1 mm (v) x 10 mm (h)).

The micro-diffraction set up is schematically shown in Fig 6, with an optical microscope image of the linear BFL used for focusing x-rays. The vertical focusing BFL was used to produce a 1 μm (vertical) x 50 μm (horizontal) beam at the sample position. The focal spot size was determined by source demagnification, the actual diffraction-limited resolution of the lens is ~ 0.3 μm . Because the confinement occurred only in the vertical direction, it was advantageous to use an unfocused wide horizontal beam to integrate over larger sample area for enhanced signal. The extensive use of x-ray slits (S₁-S₄) upstream of the sample and an evacuated 1.25-meter flight path after the sample reduces background scattering in the small angle region ($q_{\text{min}} \sim 0.01$), where the smectic layering peaks occur.

The gap size in the rectangular capillaries ranged from 20 μm – 100 μm . The microbeam was positioned at the desired sample region based on x-ray transmission images of the sample cell,

which were collected by scanning the capillary through the x-ray. Using this method, we were able to collect x-ray diffraction data at well defined positions in the sample volume, with a spatial resolution of order of a micron, to investigate the structural variations as a function of the distance from the confining surface. In Fig. 5, we present x-ray diffraction data (recorded on an image plate detector) from two sections (marked by arrows in Fig. 6b) of the SDS sample. The diffraction pattern on the left was taken from the sample near the center of the capillary while the image on the right corresponds to a 1 μm section of the sample right on the inner surface of the top capillary wall. Clearly, the smectic layers in both sections were strongly aligned parallel to the confining surfaces (the “c” orientation as shown in Fig. 2). However, it can be seen that the sample was better aligned (peaks sharper) near the surface than in the center. This is confirmed by plotting the x-ray intensity on the diffraction ring, as shown in Fig. 6, which depicts five in plane ϕ -scans corresponding to diffraction data taken at 10 μm intervals starting from the

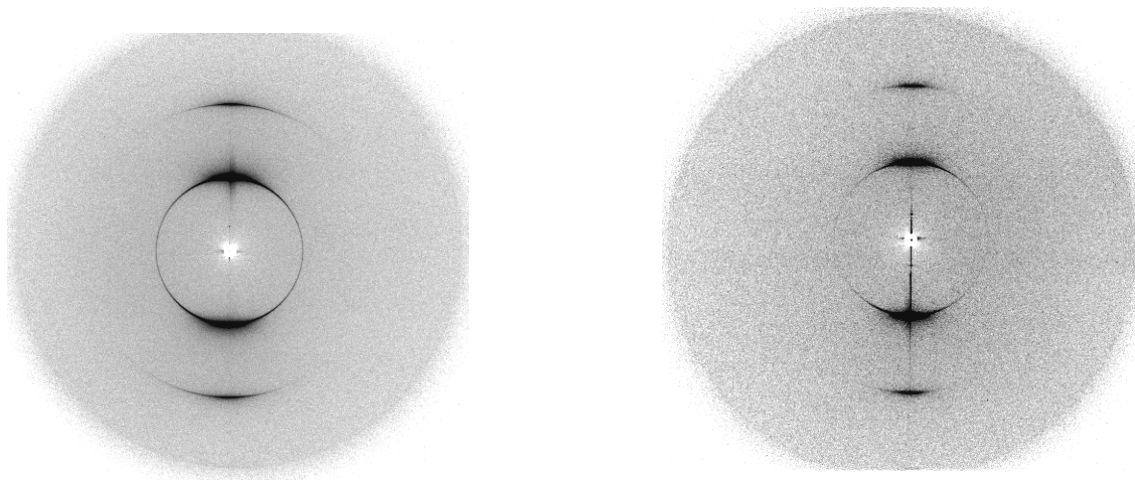


Fig. 5 Diffraction data (image plate) of the SDS sample at two positions in the capillary. The pattern on the left corresponds to the sample near the center of the capillary whereas the pattern on the right corresponds to the sample near the surface. The vertical streak of intensity seen on the image on the right is an artifact caused by residual slits scattering.

surface. The data reveal a clear sharpening of the orientation peak (better alignment) going from the center towards the edge of the capillary. This is consistent with the expectation that the surface alignment effect becomes stronger closer to the surface. This preliminary experiment opens up the possibility of combining the x-ray microprobe with the XSFA to further investigate the structural changes induced by shear. This new capability will provide the unambiguous experimental evidence for the surface layer formation and growth model discussed earlier.

5. Conclusion

We studied the confinement- and shear-induced structural changes in a SDS surfactant lamellar fluid using a second generation X-ray Surface Forces Apparatus (XSFA-II) and x-ray micro-diffraction methods. At low shear rate, we observed the separation and growth of a surface layer

from the bulk sample. Using a 1 μm x-ray microprobe, we mapped in micron-size sections the orientational distribution of the SDS sample confined in a flat x-ray capillary and showed that the smectic layers were better aligned near the surface than in the center of the capillary.

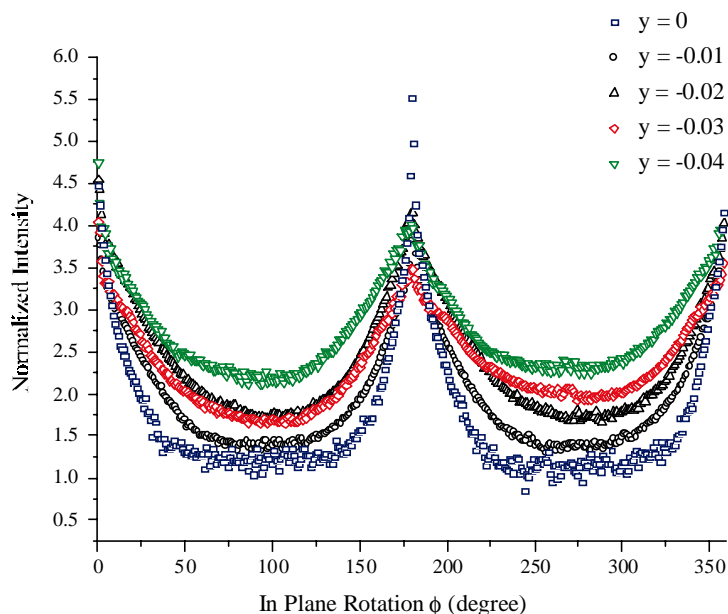


Fig. 6 In plane intensity profiles of SDS lamellar fluid mapped at five different positions in the confinement gap. The surface (inner wall of capillary) is at $y = 0$ (mm).

6. Acknowledgement

This work is supported by ONR N00014-00-1-0214, NSF DMR-9625977, the UC/Los Alamos Research (CULAR) program (STB-UC: 99-216) and University of California UC-Biotech program (99-14). Use of the APS was supported by U.S. Department of Energy, Basic Energy Sciences, Office of Energy Research, under Contract No. W-31-109-Eng-38.

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